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Cincinnati, Ohio

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LIME PRECIPITATION IN MUNICIPAL WASTEWATERS

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and
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Liming of D. C. raw or treated wastewater to *p*H 10 insolubilized the various forms of phosphorus in the wastewater, but removals to residuals of 0.3 mg./liter as P occurred only above *p*H 11.5, where precipitated magnesium hydroxide flocculated the turbidity. Nitrification of the wastewater during biochemical (secondary) treatment reduced the lime requirement for precipitation, the amounts of sludge from precipitation, and also improved phosphorus removals. Liming of organic free solutions insolubilized mixtures of ortho and polyphosphates by *p*H 10, although insolubilization of meta or tripolyphosphate alone required a *p*H above 11. The degree of biochemical oxidation significantly influenced the phosphorus removals, while temperature and ionic strength did not.

The removal of the nutrients, phosphorus and nitrogen, as well as the organic carbon from wastewaters is necessary if the rapid eutrophication of lakes and the degradation of streams is to be prevented. Alkaline precipitation by lime with flash mixing, flocculation, and sedimentation is a practical method of removing phosphorus and particulate organics. The process at high *p*H also may permit the air stripping (*4*) of ammonia.

Lime precipitation has been demonstrated at the FWPCA-DC Pilot Plant (*10*) in Washington, D.C., at the FWPCA Advanced Waste Treatment Pilot Plant (*1*) in Lebanon, Ohio, and at the South Lake Tahoe Public Utility District Water Reclamation Plant (*4*) in California. These plants successfully used the lime process as tertiary treatment of municipal secondary effluent.

At Lebanon, Ohio, the lime addition into a wastewater with high alkalinity (~ 350 mg./liter as calcium carbonate) in single-stage precipitation with sedimentation and filtration successfully removed total phosphorus to less than 0.5 mg./liter as P by *p*H 9.5 to 10. In Washington, D.C., and Lake Tahoe, California, the lime process in wastewaters of moderate alkalinities (100 to 150 mg./liter as calcium carbonate) employed two-stage precipitation and sedimentation at high *p*H (11 to 12) with intermediate recarbonation. In typical high *p*H treatment (*10*) of secondary effluents, precipitation by lime above *p*H 11.5 with sedimentation at overflow rates up to 1,500 gal./sq. ft./day followed by recarbonation, sedimentation, and filtration reduced the total phosphorus to less than 0.30 mg./liter (95% removal) and the organic carbon (TOC) to less than 15.0 mg./liter. The calcium carbonate sludges were easily dewatered to 40% solids and could be recalcined to recover the lime.

In the process, the lime addition precipitates the gelatinous calcium hydroxylapatite, granular calcium carbonate, and, at high *p*H, magnesium hydroxide from the water [Equations (1) to (3)]. These precipitates along with the particulate organics are flocculated and settled to remove phosphorus and organic carbon. The calcium carbonate increases the floc densities and permits high overflow rates in the sedimentation basin. The magnesium hydroxide, as a flocculant, improves the liquid-solids separation:

$$Ca^{++} + HCO_3^- + OH^- \longrightarrow CaCO_3 + H_2O \quad (1)$$

$$5Ca^{++} + 7OH^- + 3H_2PO_4^- \longrightarrow Ca_5(OH)(PO_4)_3 + 6H_2O \quad (2)$$

$$Mg^{++} + 2OH^- \longrightarrow Mg(OH)_2 \quad (3)$$

In the high *p*H lime process, the excess calcium ions from the lime may be precipitated with carbon dioxide [Equation (4)] in a recarbonation basin and settled in a

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second sedimentation basin, or may be precipitated in the first stage with Na_2CO_3 [Equation (5)]:

$$Ca^{++} + 2OH^- + CO_2 \longrightarrow CaCO_3 + H_2O \quad (4)$$

$$Ca^{++} + 2Na^+ + CO_3^= \longrightarrow CaCO_3 + 2Na^+ \quad (5)$$

In the single stage sodium carbonate system, or if additional *p*H reduction is desired in the two stage process, carbon dioxide is employed to neutralize the hydroxide ions [Equation (6)]:

$$OH^- + CO_2 \longrightarrow HCO_3^- \quad (6)$$

In wastewaters, the organics, organic phosphorus, and polyphosphates produce more complex reactions than the simplified equations. Limited information (*2, 11*) is available on the complex mechanism of the precipitation and more importantly on the distribution of particulate and soluble components during precipitation. The effects of wastewater characteristics on the process and the evaluation of the distribution of particulate and soluble components over a wide *p*H range, however, are not clearly defined. The objectives of this study were to establish the distribution of the particulate and soluble components during precipitation for a wide *p*H range and to determine the effect of various wastewater characteristics on process.

RESEARCH APPROACH

In the lime precipitation of municipal wastewaters, the important variables are alkalinity and bicarbonate concentration, the type and quantity of phosphorus, calcium concentration, magnesium concentration, the type of organic and the degree of biological treatment, ionic strength, and temperature. In municipal wastewaters, these variables fluctuate not only with the source of the wastewater and type of conventional treatment but also with diurnal and seasonal changes.

A group of wastewaters and synthetic solutions were selected to provide a wide variation of the above variables. The selected wastewaters and solutions included:

1. Organic free solutions that had ion inventories identical to the District of Columbia's wastewater.
2. Raw wastewater from the District of Columbia's plant.
3. Secondary effluent from the District of Columbia's modified aeration plant [Sludge Retention Time (SRT) = 1 day, Mixed Liquor Suspended Solids (MLSS) = 500 mg./liter, and 2 hr. aeration time).
4. Nitrified effluent from a bench scale unit, batch fed with District of Columbia primary effluent (SRT = 10 days and MLSS = 2,500 mg./liter).
5. Extended aeration effluent from a bench scale unit, batch fed with District of Columbia primary effluent (SRT = 40 days and MLSS = 2,500 mg./liter).
6. Secondary effluent from the District of Columbia's plant with added ions to simulate wastewaters with increased ionic strength.

In the study, these selected waters were treated with lime in laboratory jar tests. In the standard jar test, multiple 1 liter samples were dosed with an increasing amount of high calcium (98% calcium oxide) lime and flash mixed for 1 min. at 100 rev./min. The solution was flocculated for 15 min. at 30 rev./min. and then settled for 30 min. before the decant was siphoned for analysis. A portion of the decanted sample was filtered through a 0.45 μ membrane filter to separate the unsettleable particulate components from the dissolved components. The 0.45 μ membrane filter was selected because bacterial size particles and larger were removed. The smaller pore size filters (0.22 and 0.10 μ) easily clogged and did not increase solids or phosphorus removal from the decant.

The filtered portion of the decant was analyzed for total phosphorus, orthophosphate, calcium ion, magnesium ion, and phenophthalein and methyl orange alkalinity. The unfiltered decant was analyzed for *p*H, turbidity, suspended solids, conductivity, total organic carbon (TOC), total phosphorus, orthophosphate, calcium ion, and magnesium ion.

The total phosphorus was determined by digesting to orthophosphate with the potassium persulfate method (*6*). The orthophosphate was determined by procedures (*8*) in the "National Water Quality Network Operating Manual." The calcium and magnesium concentrations were determined on a Perkin-Elmer Model 303 Atomic Adsorption Spectrophotomer. The total organic carbon (TOC) was measured on a Beckman Carbonaceous Analyzer (*16, 17*) equipped with a IR315 infrared analyzer. The glass fiber filter method (*19*) was used for the suspended solids. The remainder of the analytical work employed procedures in the twelfth edition of "Standard Methods" (*12*).

The distribution of the components in the settled decant was obtained by comparing the analyses of the unfiltered decant, which contained unsettleable particulates and soluble components, to the filtered decant, which contained only the soluble portion. As appropriate, the results of the laboratory jar tests were also compared to the performance of the FWPCA-DC Pilot Plant.

ALKALINITY, HARDNESS, AND PHOSPHORUS REMOVAL

The chemical reactions in wastewaters during lime precipitation are *p*H dependent and thus are related to the alkalinity of the wastewater. Usually, wastewater alkalinities measure bicarbonate-carbonate, acid phosphate-phosphate, and ammonium-ammonia buffer capacities. In municipal wastewater, the bicarbonate normally contributes the major buffering capacity. In

wastewater from surface water supplies, the alkalinity typically varies between 100 and 150 mg./liter as equivalent calcium carbonate. In regions with limestone rock or underground water supplies, the alkalinity, however, increases sharply and may exceed 500 mg./liter as calcium carbonate.

In lime precipitation of wastewater, the buffer capacities [Equations (7) to (9)] controlled the *p*H after lime addition by neutralizing the hydroxide ions from the calcium hydroxide:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \quad (7)$$

$$H_2PO_4^- \rightleftharpoons 2H^+ + PO_4^= \quad (8)$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad (9)$$

Thus, the lime dose required to overcome the buffer capacity increased with increasing alkalinity (Figure 1) of the wastewater.

Phosphorus removal, as illustrated in the wastewaters from the District of Columbia (Figures 2, 3, and 4), increased as the *p*H of the water increased and, for higher wastewater alkalinities, required more lime. The phosphorus removal was, however, a combination of two processes, the insolubilization of the various forms of phosphorus and the physical separation of the particulate phosphorus from the water. Thus, while the total

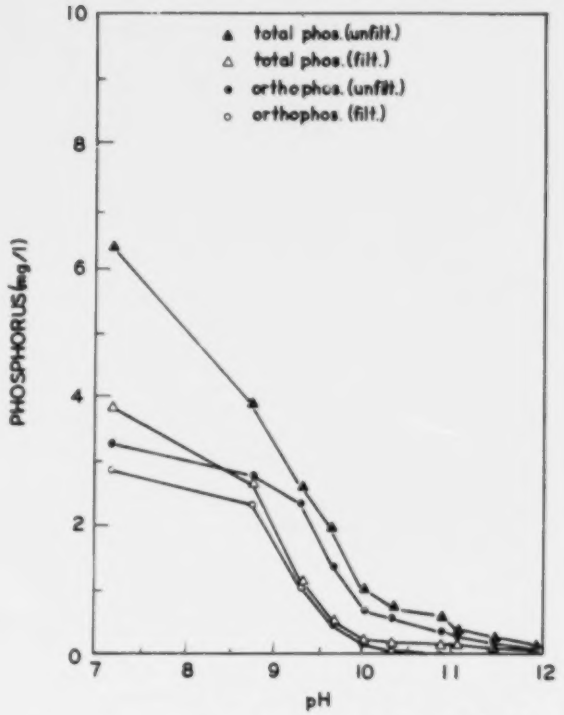

Fig. 2. Lime precipitation and phosphorus removal from raw wastewater.

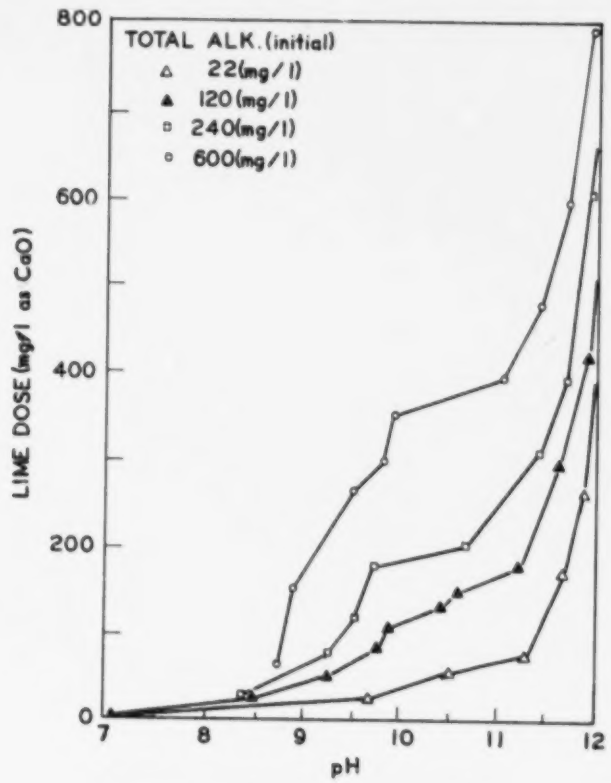

Fig. 1. Alkalinity, lime dose, and *p*H.

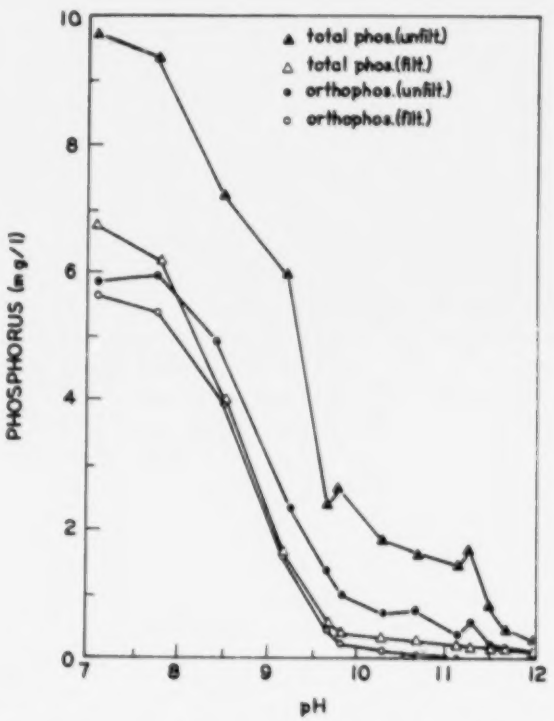

Fig. 3. Lime precipitation and phosphorus removal from secondary effluent.

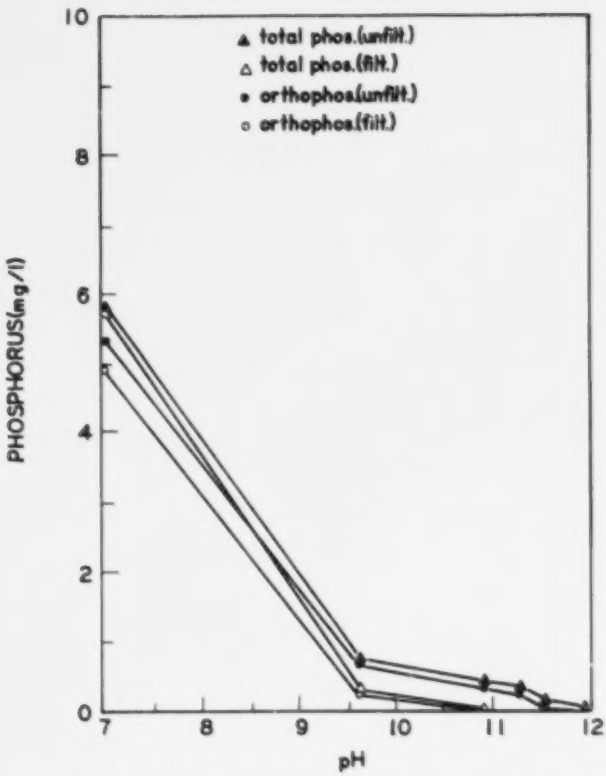

Fig. 4. Lime precipitation and phosphorus removal from nitrified effluent.

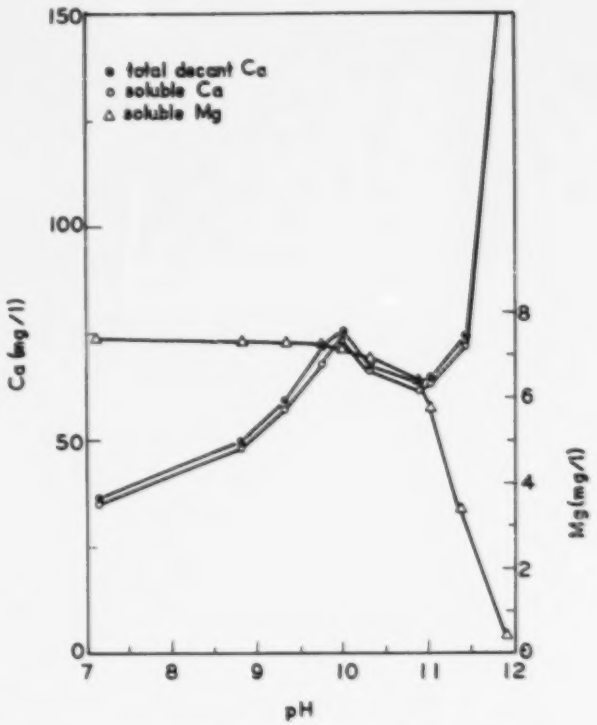

Fig. 5. Lime precipitation and calcium and magnesium concentrations in raw wastewater.

soluble phosphorus in water of moderate alkalinities (100 to 150 mg./liter as calcium carbonate, District of Columbia wastewater) was reduced to less than 0.3 mg./liter as P at *p*H 10, the total residual phosphorus (dissolved and unsettleable particulate) was not reduced by sedimentation to less than 0.3 mg./liter as P until above *p*H 11.5.

The phosphorus removal behavior in the laboratory tests was confirmed by the precipitation units in the FWPCA-DC Pilot Plant. Below *p*H 11.5, total phosphorus residuals in the overflow from the pilot scale sedimentation usually exceeded 2 mg./liter as P unless a supplemental flocculant such as ferric hydroxide was added to the water. In addition, without the flocculant (ferric hydroxide) the residual turbidity and thus the residual phosphorus was not efficiently removed by dual media filtration.

The residual concentrations of calcium and magnesium ions (hardness) during lime addition provided further insight into the precipitation process. Both the total residual (unsettleable particulate and soluble) and soluble (filtered) calcium concentrations (Figures 5, 6, and 7) increase only gradually with lime dose up to *p*H 10 because part of the calcium from the lime precipitated the phosphates and carbonates from the water and was removed by settling. Above approximately *p*H 10, the residual

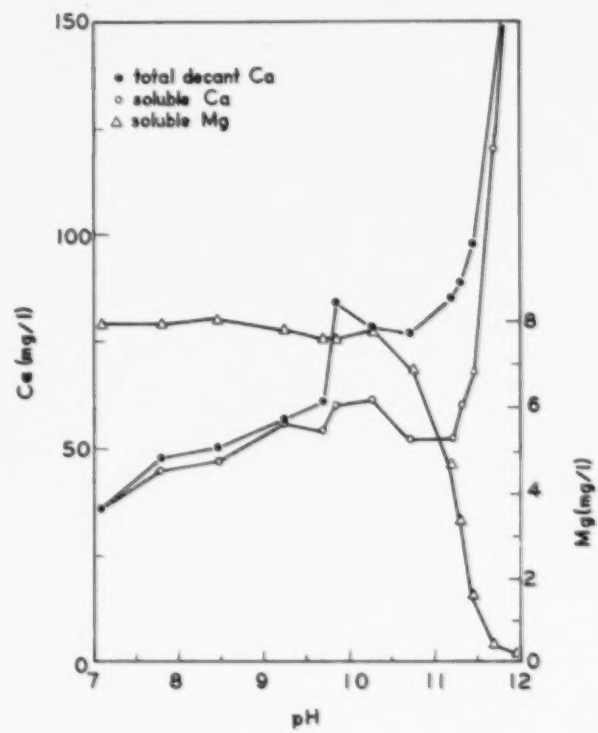

Fig. 6. Lime precipitation and calcium and magnesium concentrations in secondary effluent.

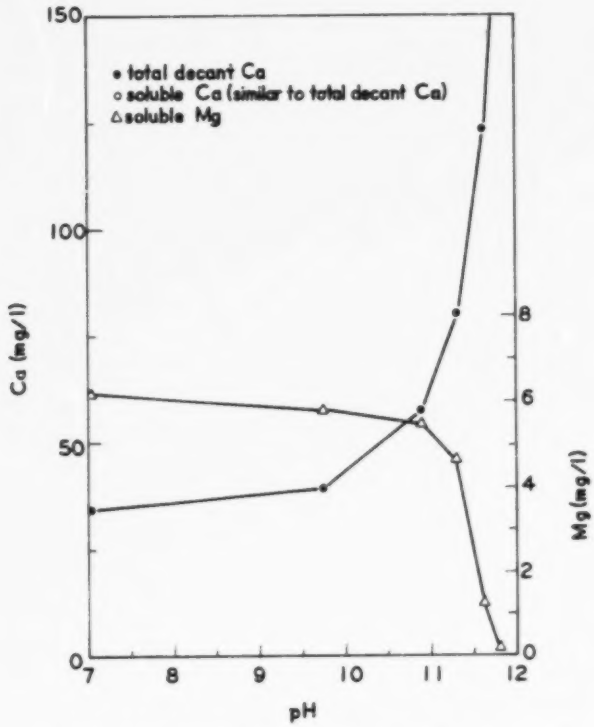

Fig. 7. Lime precipitation and calcium and magnesium concentrations in nitrified effluent.

calcium (total and soluble) decreased even though lime (calcium hydroxide) was being added and the phosphate precipitation was essentially completed. This decrease in the residual calcium concentration occurred because the major portion of the bicarbonate alkalinity precipitated from the water as calcium carbonate. Above *p*H 11.5, the bicarbonate alkalinity was nearly completely precipitated, and additional lime proportionately increased the residual calcium ion concentration in the decant.

Calcium balances around the precipitation system indicated that at *p*H 10 about 25 mg./liter of the precipitated calcium ion was as calcium carbonate (~ 60 mg./liter of calcium carbonate). The solubility of calcium carbonate and the bicarbonate-carbonate equilibrium indicated that most of the bicarbonate alkalinity should have been precipitated as calcium carbonate (~ 180 mg./liter) by *p*H 10. Van Wazer (*18*) has suggested the reason for the inhibition of the carbonate precipitation in solutions containing phosphorus is that the phosphorus absorbed onto the growing faces of the calcium carbonate nuclei prevented further crystal growth and thus inhibited the precipitation of the calcium carbonate.

Indeed, the sludge produced in tests below *p*H 10 was gelatinous and did not exhibit the characteristics of a calcium carbonate sludge. With the phosphorus interference removed by *p*H 10, the calcium carbonate then precipitated with increasing lime addition, and the sludge exhibited the grainy appearance of calcium carbonate.

The FWPCA-DC Pilot Plant Studies (*2, 10*) revealed that the complete precipitation of the bicarbonate alkalinity as calcium carbonate was necessary in the District of Columbia wastewater to permit high overflow rates and filterable residual turbidity. In contrast, in wastewaters with high alkalinities (350 mg./liter), such as those at Lebanon, Ohio, sufficient calcium carbonate precipitated in the *p*H range between 9.5 to 10 to produce sludge with satisfactory calcium carbonate characteristics (*1, 3*). Lime precipitation in these higher alkalinity waters also produced residual turbidities in the *p*H range between 9.5 to 10 that were filterable with the dual media filter.

The soluble calcium compared to the total residual calcium concentration in the decant, especially in the winter in the D. C. secondary (Figure 6), indicated that the unsettleable precipitate (visual haze) in the limed wastewater contained calcium precipitates. This unsettleable haze also included phosphate precipitates and thus reduced the phosphorus removal efficiency. The amount of haze in the decant was variable and was usually eliminated above *p*H 11.5. Lime treatment of higher quality D. C. secondary effluents (Figure 7) and D. C. raw wastewater (Figure 5) produced much less haze than that in lower quality secondary effluents.

The magnesium ion concentrations during lime addition (Figures 5, 6, and 7) indicated that in all D. C. wastewaters efficient clarification and phosphorus removal, observed above *p*H 11.5, occurred as the natural magnesium ion in the wastewater precipitated as magnesium hydroxide. The magnesium hydroxide was the necessary flocculant to clarify the water and to improve phosphorus removal. In the D. C. wastewater, the magnesium precipitation was essentially completed by a *p*H between 11.5 and 11.8.

In D. C. wastewater, a fivefold proportioned increase in ionic strength but without increases in phosphorus or magnesium concentrations increased the alkalinity and hardness of the wastewater but did not significantly alter the insolubilization of the total phosphorus nor its removal by sedimentation (Figure 8). The total residual phosphorus in the decant was reduced to less than 0.3 mg./liter as P by *p*H 11.5.

ORTHOPHOSPHATE REMOVAL

In wastewaters, the phosphorus exists as orthophosphate, polyphosphate, and organic phosphorus. In most wastewaters the chief form of phosphorus is orthophosphate which in the lime process precipitates as calcium hydroxylapatite (*13*). Normally, in the District of Columbia raw wastewaters, the orthophosphate comprised 55 to 70% of the total phosphorus and in the secondary effluent (modified aeration) 65 to 75%. In the nitrified D. C. secondary effluents, 95% or more of the total phosphorus was

orthophosphate; in the extended aeration effluent it was almost entirely orthophosphate.

Lime precipitation in raw wastewater, secondary effluent, nitrified effluent, and organic free solutions (one containing orthophosphate and one containing 10% pyro, 10% tripoly, 10% meta, and 70% orthophosphate) exhibited essentially similar precipitation of the dissolved orthophosphate. In all cases, the residual soluble orthophosphate was less than 0.3 mg./liter as P by *p*H 10.0 regardless of different initial concentrations (Figure 9). The presence of organics or polyphosphates did not significantly change the precipitation behavior of orthophosphate.

Temperature variations from 9° to 26°C. with the 15 min. flocculation period in the tests did not alter either the precipitation of orthophosphate or the settling behavior of the precipitated orthophosphate. The soluble orthophosphate was precipitated to less than 0.3 mg./liter as P by *p*H 10.0 at all temperatures. The settling behavior of the orthophosphate precipitate also was not significantly changed over the 9° to 26°C. temperature range for all wastewaters and synthetic solutions.

A fivefold increase in ionic strength in the District of Columbia secondary effluent increased the *p*H required to precipitate the soluble orthophosphate to less than 0.3 mg./liter as P from below *p*H 10 to approximately *p*H 10.5. Orthophosphate residuals in the high ionic strength system after sedimentation, however, were similar to those in the normal District of Columbia wastewater with the residual in the decant reduced to 0.3 mg./liter by *p*H 11.5.

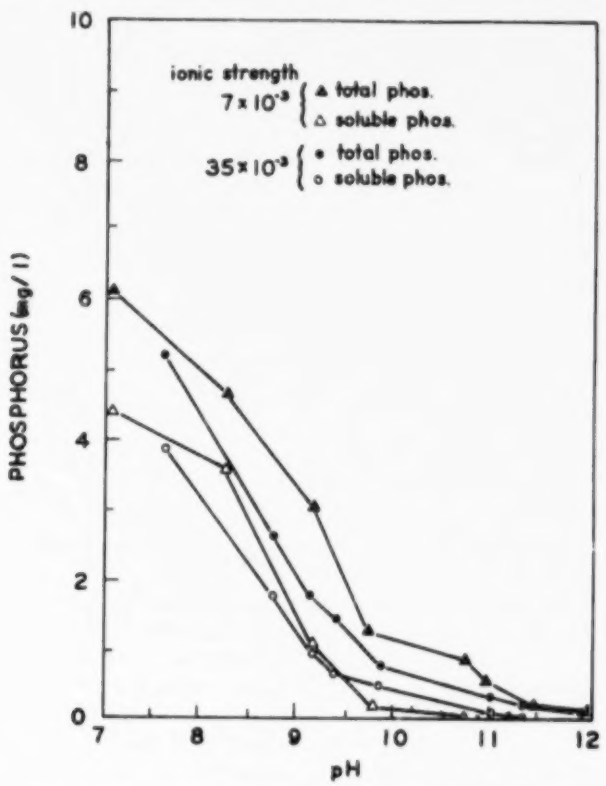

Fig. 8. Phosphorus removal from secondary effluent with varied ionic strengths.

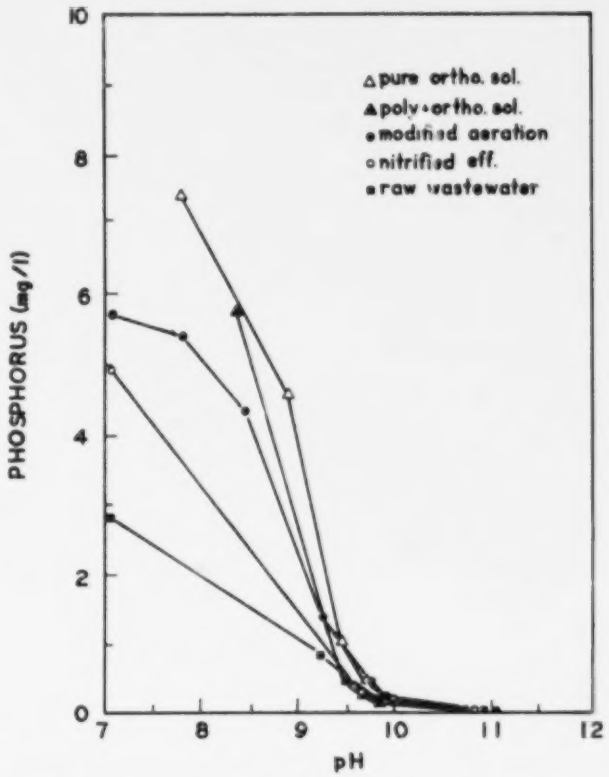

Fig. 9. Orthophosphate precipitation in various wastewaters and synthetic solutions.

POLYPHOSPHATE REMOVAL

The polyphosphates, employed as builders in detergents, include three forms: metaphosphate, tripolyphosphate, and pyrophosphate. Polyphosphates do not usually exceed more than 10% of the phosphorus in municipal raw sewage (*5*) and during secondary treatment are almost completely hydrolyzed to orthophosphate. Metaphosphate is the most readily hydrolyzed of the three, followed by tripolyphosphate, and then pyrophosphate (*15*). The polyphosphates also inhibit calcium carbonate precipitation more than pure orthophosphate (*11*). With their low concentrations in most wastewaters, tests of the polyphosphate effects on lime precipitation are best conducted on synthetic solutions.

In organic free solutions with ion inventories similar to District of Columbia wastewater but with only the meta or the tripolyphosphates, soluble phosphorus removals increased only slowly below *p*H 9.5 and then in-

creased sharply with increasing *p*H (Figures 10 and 11). Reduction of the soluble residual to 0.3 mg./liter as P occurred only above *p*H 11.5. Settled residuals less than 0.3 mg./liter as P occurred only above *p*H 12.0. For pyrophosphate, removals (Figure 11) increased sharply with increasing *p*H even below *p*H 9.5, and soluble residuals of 0.3 mg./liter as P occurred by *p*H 11.0. Again, however, a settled residual less than 0.3 mg./liter as P occurred above *p*H 12.0. The precipitated solids in the individual polyphosphate systems also exhibited poor settling behavior.

The observed calcium removals (Figures 12 and 13) suggested that the meta and tripolyphosphates were removed from solution either by adsorption on the precipitating calcium carbonate and magnesium hydroxide or by hydrolysis to orthophosphate and subsequent precipitation as calcium hydroxylapatite. In fact, the removal mechanism for meta and tripolyphosphates may have been a combination of adsorption on the calcium and magnesium precipitates and hydrolysis with subsequent precipitation as calcium hydroxylapatite.

Unlike the nearly complete solution of the meta and tripolyphosphates in organic free water, only 4 of the 8 mg./liter of pyrophosphate added to the organic free system dissolved before lime addition. The 4 mg./liter of pyrophosphate in solution may have produced less inhi-

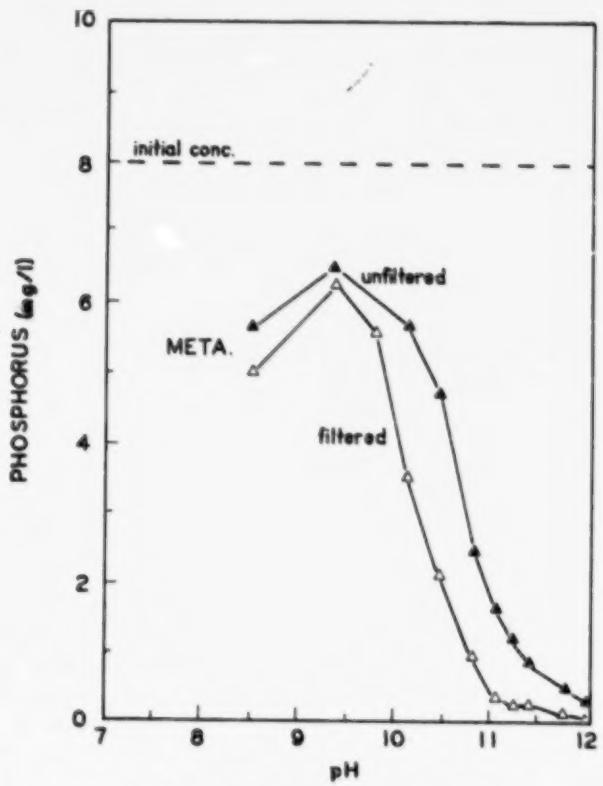

Fig. 10. Metaphosphate removal.

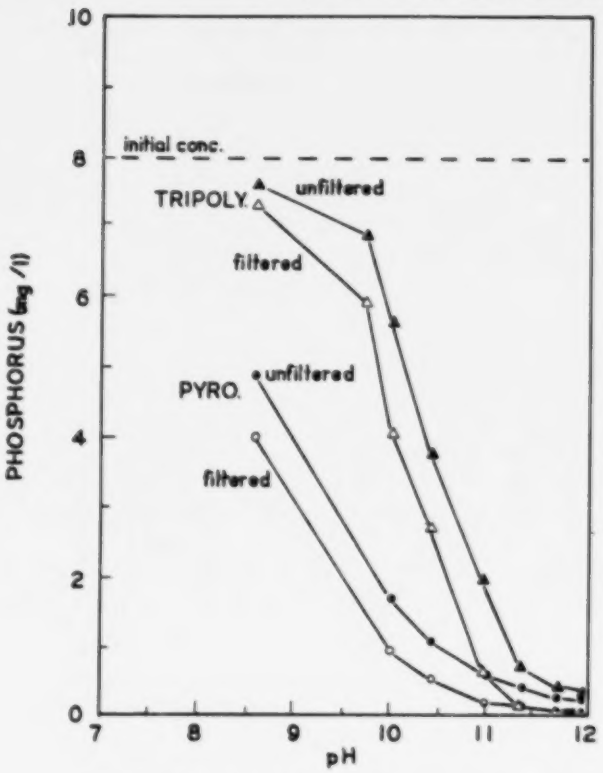

Fig. 11. Tripoly and pyrophosphate removals.

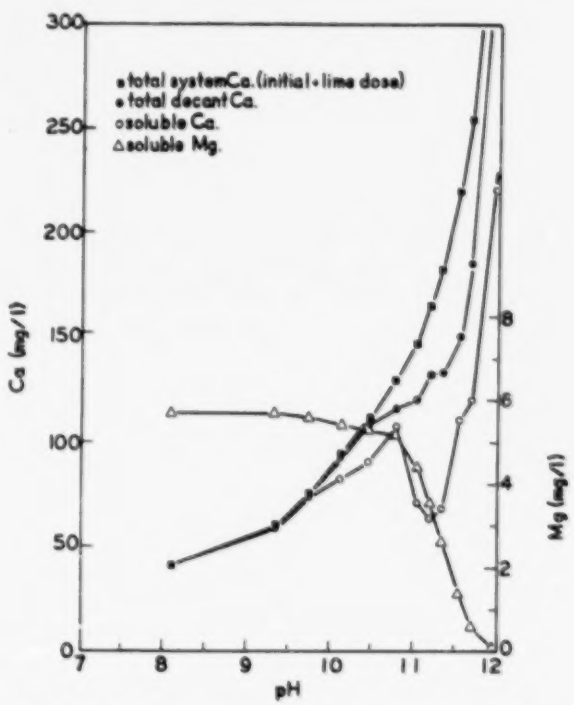

Fig. 12. Calcium and magnesium concentrations during a metaphosphate removal.

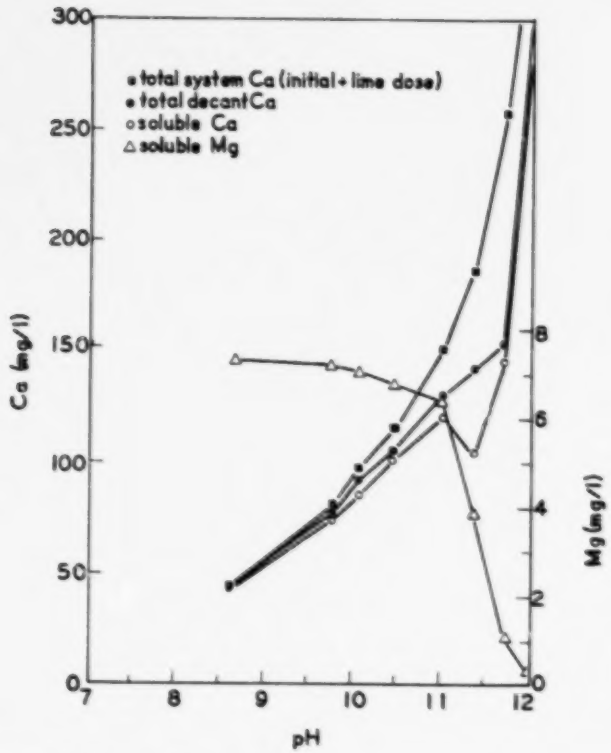

Fig. 13. Calcium and magnesium concentrations during tripolyphosphate removal.

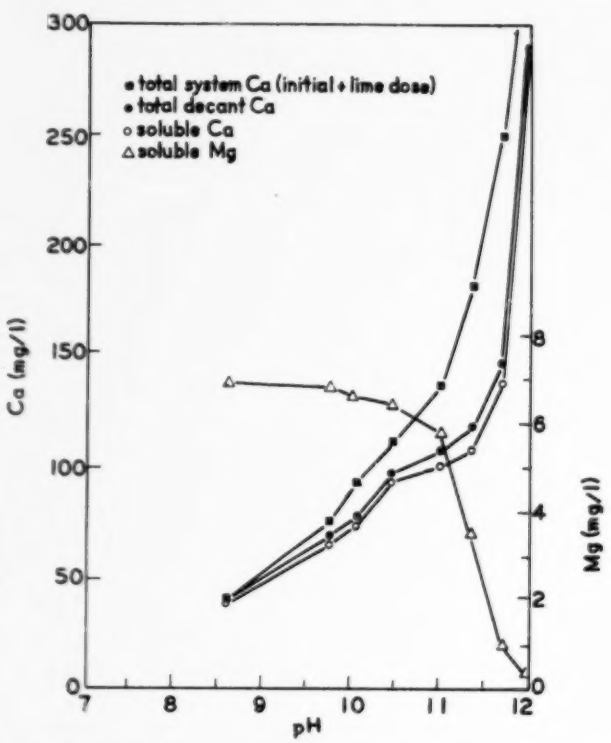

Fig. 14. Calcium and magnesium concentrations during pyrophosphate removal.

bition of the calcium carbonate precipitation and thus have been adsorbed on the precipitating calcium carbonate at lower *p*H than meta and tripolyphosphates (Figure 14). These limited studies on the polyphosphate systems, however, were not detailed enough to confirm the suggested mechanisms for polyphosphorus insolubilization.

In an organic free solution with a soluble phosphate mixture of meta (10%), tripoly (10%), and ortho (70%), lime addition produced total soluble phosphorus removals and settling behavior similar to that in solutions containing only orthophosphate (Figure 15). The total soluble residuals were less than 0.3 mg./liter as P by *p*H 10.0, and the total settled phosphorus residuals were less than 0.3 mg./liter as P by *p*H 11.0. Only a slight reduction in settleability of the mixture was observed in the *p*H range of 9.7 to 10.7 compared with the settleability of the pure orthophosphate system.

In the mixed phosphate solutions at *p*H 10.0, the precipitates, a combination of calcium carbonate and calcium hydroxylapatite, were sufficient to remove and settle the polyphosphates. The polyphosphates in this mixture also did not noticeably inhibit calcium carbonate precipitation to any greater degree than the same quantity of orthophosphate. Tests in the District of Columbia raw wastewater (Figure 2), exhibited similar behavior to

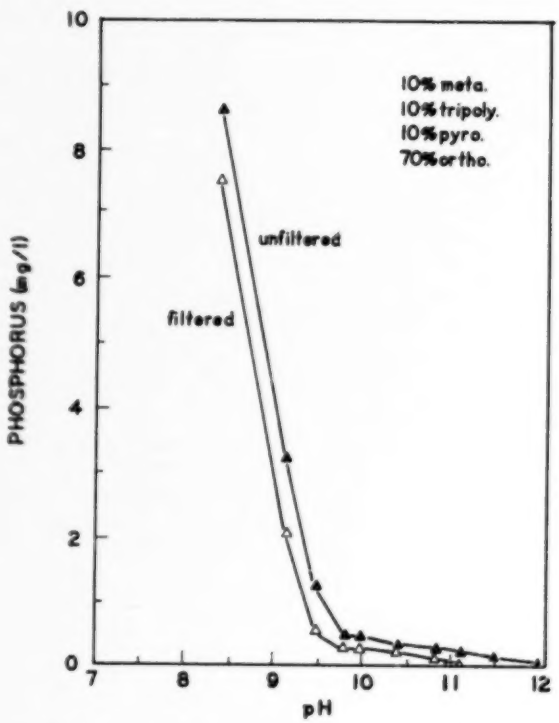

Fig. 15. Phosphate removal in a solution of ortho and polyphosphate.

the organic free solutions. Therefore, polyphosphates at concentrations normally found in District of Columbia raw wastewater did not interfere with phosphorus removal by the lime process.

ORGANIC PHOSPHORUS REMOVAL

In wastewater, the organic phosphorus, either in organic fragments or in the biological mass, is almost entirely particulate and is removed with the removal of suspended solids (9). The organic phosphorus, however, is not easily analytically separated from the polyphosphorus because the analytical separation of the organic phosphorus and polyphosphates is a function of an arbitrary hydrolyzing procedure (5). Thus, in the study, phosphorus was measured as total or orthophosphate. The difference between total phosphorus and orthophosphate represented both organic phosphorus and polyphosphates, and the removal of organic phosphorus was only indicated by removal of total phosphorus.

The type and amount of organic phosphorus in the wastewater varied with the degree of conventional treatment. In the District of Columbia raw wastewater, 30 to 45% of the phosphorus occurred as an unknown combination of polyphosphates and organic phosphorus. The amount of organic phosphorus in the secondary effluent was variable and depended upon the efficiency of aeration and secondary sedimentation. The organic phosphorus was incorporated in the unsettled biologically active solids. After aeration, little polyphosphate should have been present (5).

Lime precipitation in the raw wastewater produced consistent removals of total phosphorus and therefore of organic phosphorus. The removals were independent of seasonal or diurnal variation. Above *p*H 11.5 the magnesium hydroxide precipitated and coagulated the particulate organics, calcium hydroxylapatite, and calcium carbonate (Figures 2 and 3). Efficient liquid-solids separation to total phosphorus residuals of 0.3 mg./liter occurred above *p*H 11.5 in all tests on the raw wastewater. The 5 to 10 mg./liter of magnesium ions in the wastewater was sufficient to produce good clarification.

Secondary effluent from the District of Columbia's modified aeration process exhibited similar ortho and total phosphate insolubilization (below 0.3 mg./liter as P by *p*H 10.0) as in the raw wastewater (Figure 4). The District of Columbia's secondary effluent, however, exhibited poorer liquid-solids separation than in the limed raw wastewater. Turbidity even at high *p*H's remained in the decant in cold weather. Even at *p*H 11.7, with essentially all the magnesium hydroxide precipitated, residuals greater than 0.3 mg./liter as P of total phosphorus occasionally occurred.

Microscopic examination revealed the unsettleable turbidity was single dispersed spherical bacteria (Figure 16). In the winter the biological kinetics in the cold

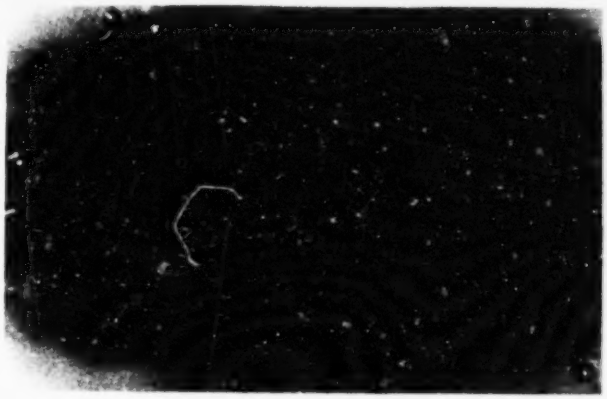

Fig. 16. Bacterial haze in limed secondary effluent.

water (8°C.) slowed, and poor bioflocculation resulted. Singular bacteria persisted through tertiary clarification and filtration. These bacteria, in the log growth phase of the modified activated sludge process, inhibited coagulation and clarification and decreased total phosphorus removals from effluent. In the warmer (> 20°C.) water of summer, the bacteria showed strong self-motility even after 4 hr. at *p*H 12.0 but were better bioflocculated and did not prevent efficient phosphorus removal.

Nitrified activated sludge and extended aeration effluents were limed to observe the behavior of higher quality secondary effluents. These aeration processes had low metabolisms and were characterized by good bioflocculation which produced lower effluent suspended solids and also lower percentages of organic phosphorus in the solids. Both systems, when treated with lime, behaved as the organic free pure orthophosphate system with only a slight increase in the suspended solids in the decant. The organic solids were coagulated and efficiently settled with the precipitation of magnesium hydroxide (Figures 6 and 7).

In the biological conversion of ammonia to nitrates, nitric (HNO_3) acid was produced by the nitrification (7, *14*) [Equation (10)] in the wastewater:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O \qquad (10)$$

Since electrical neutrality in the water is always maintained and the formation of nitrate (NO_3^-) from ammonia produced negative charges and removed positive charges (NH_4^+), the net increase in negative charges was balanced by the formation of positive hydrogen ions (H^+). The hydrogen ions reacted with the bicarbonate buffer capacity in the water to form carbonic acid and thus removed negative and positive charges from the system.

Fourteen milligrams per liter of ammonia nitrogen biologically converted to nitrate produced sufficient acid to convert approximately 100 mg./liter of bicarbonate alkalinity as calcium carbonate to carbonic acid [Equation (11)]:

$$2HCO_3^- + 2H^+ \longrightarrow 2H_2CO_3 \qquad (11)$$

This reduction of buffer capacity reduced lime requirements (Figure 1) for phosphorus removal from the nitrified District of Columbia wastewaters and also eliminated nearly all of the precipitated calcium carbonate (Figure 7).

Although the nitrifying autotrophs use carbon dioxide as a source of cell carbon, McCarthy's (7) cell synthesis values for nitrification indicated that not more than 15% of the bicarbonate carbon leaving the system during nitrification could have been incorporated in the nitrified cellular mass. Therefore, the alkalinity reduction must have chiefly occurred by carbon dioxide stripping in the aeration process.

ORGANIC REMOVAL

In addition to phosphorus removal, the lime process also removed organic carbon (Table 1). The organic carbon existed in three forms: raw organic fragments, biological cells, and dissolved organics. With efficient clarification, the lime process removed organic fragments and biological cells. The amount of adsorption of dissolved organics on the precipitate was not known, but dissolved organic carbon residuals remained in the decant.

In the raw wastewater, the organic carbon was not assimilated and converted into biological cells (activated sludge) and was mostly in the forms of raw organic fragments and dissolved organics. Despite a wide variation in the suspended solids in the District of Columbia raw wastewater, the total organic carbon (TOC) was reduced to a residual level of approximately 20 mg./liter in all the tests. The lime treated raw wastewater above *p*H 11.5 had a consistently clear low turbidity decant (< 2.0 J.t.u. with suspended solids of 10 mg./liter).

As previously indicated, the organic carbon in the secondary effluent from modified aeration at the District of Columbia contained motile bacteria that in cold weather were poorly bioflocculated. The poorly bioflocculated bacteria hindered coagulation and thus also reduced organic removal efficiency. In the summer, during periods with satisfactory bioflocculation, the organic carbon was reduced to 9 mg./liter of TOC, 10 mg./liter of suspended solids, and less than 2.0 J.t.u. of turbidity; but in the winter, with decreased bioflocculation, residuals of 15 mg./liter of TOC, 20 mg./liter of suspended solids, and 5.0 J.t.u. of turbidity occurred. Similar results also occurred in the FWPCA-DC Pilot Plant.

Nitrified effluents were low in suspended solids. The metabolism of these systems promoted good bioflocculation and sedimentation. The bacteria were in the declining growth phase. Higher order animals such as the stalk ciliate, free swimming ciliates, and even rotifers improved the water quality by reducing the bacterial and organic turbidity.

TABLE 1. ORGANIC REMOVAL BY LIME PRECIPITATION

	Residual in Decant		
	T.O.C. (mg/l)	Suspended Solids (mg/l)	Turbidity J.T.U.
RAW WASTEWATER	20	10	<2.0
SECONDARY EFFLUENT[2]	9	10	<2.0
SECONDARY EFFLUENT[3]	15	20	5.0
NITRIFIED EFFLUENT	8	5	<1.0
EXTENDED AERATION	7	5	<1.0

1 lime to pH 11.5 and sedimentation
2 Modified Aeration, good bioflocculation
3 Modified Aeration, poor bioflocculation

In the lime tests on nitrified effluents, the dissolved organic carbon was reduced to 8.0 mg./liter TOC and the suspended solids to 5 mg./liter by *p*H 11.5. The residual organic solids were easily flocculated with the magnesium hydroxide with the turbidity in the decant well below 1 J.t.u.

The extended aeration effluent was similar to a nitrified effluent. A slight difference in precipitation behavior was caused by the inert solids from the increased digestion time which added a slight turbidity in the water. This turbidity was easily coagulated when the magnesium hydroxide precipitated. In the lime tests at *p*H 11.5, the dissolved organic carbon in the decant was reduced to less than 7.0 mg./liter of TOC, the suspended solids again to 5 mg./liter, and turbidity to well below 1 J.t.u.

CONCLUSIONS

The insolubilization of the various forms of phosphorus in the D. C. wastewaters and organic free solutions to less than 0.3 mg./liter as P was completed by *p*H 10. A lime dose of approximately 130 mg./liter as CaO was required to achieve *p*H 10 in water with an alkalinity of 120 mg./liter as calcium carbonate, and the dose increased as the alkalinity of the wastewater increased. In the study, temperatures from 9° to 26°C., concentrations of polyphosphorus, organic phosphorus, and organics normally found in the D. C. wastewater, the degree of biochemical oxidation in the secondary treatment, and a fivefold increase in ionic strength did not significantly change the insolubilization of the total phosphorus.

The laboratory separation of the insolubilized phosphorus from the D. C. wastewater to less than 0.3 mg./liter as P by sedimentation required the precipitation of 5 to 10 mg./liter of magnesium ions from the water as flocculant magnesium hydroxide. In raw wastewater, the separation of the solids in the static laboratory tests was independent of the initial concentration of phosphorus, the temperature, organic content, diurnal wastewater variations, and the ionic strength. The total residual

phosphorus after sedimentation was reduced by the magnesium hydroxide flocculation to less than 0.3 mg./liter as P by *p*H 11.5; the organic carbon (TOC) was reduced from about 100 mg./liter to 20 mg./liter.

In well-bioflocculated secondary effluents (nitrified or modified aeration in the summer), the separation of the insolubilized phosphorus exhibited similar or superior behavior compared with the raw wastewater. After being limed to *p*H 11.5 and settled, the residual TOC usually was less than 10 mg./liter. In the nitrified D. C. wastewater, the nitric acid produced by the nitrifying bacteria converted the bicarbonate alkalinity (HCO_3^-) to carbonic acid which was stripped as carbon dioxide from the water during the aeration process. The removal of the bicarbonate alkalinity during nitrification reduced the lime dose required to insolubilize the phosphorus at *p*H 10 to approximately 40 mg./liter as calcium oxide and produced chiefly calcium hydroxylapatite and the residual organic solids in the lime treated nitrified wastewater.

In poorly bioflocculate secondary effluent (modified aeration in the winter), a visual haze occurred and consisted chiefly of single bacteria. The haze was difficult to flocculate and occasionally increased the phosphorus and organic residuals in the limed water after sedimentation to more than 0.3 mg./liter even above *p*H 11.5. The separation efficiency of the solids from poorly bioflocculated effluents decreased more markedly in corresponding FWPCA-DC Pilot treatment and indicated that well-bioflocculated secondary effluent was needed to produce low (0.3 mg./liter) phosphorus residuals.

Two process applications were suggested by the above results. The consistent phosphorus insolubilization and removal to residuals of 0.3 mg./liter as P and the reduction in organic carbon to residuals of 20 mg./liter in the raw wastewater after lime precipitation indicate that independent physical-chemical treatment may be a substitute for conventional tertiary treatment. The independent physical-chemical treatment would consist of high *p*H lime precipitation, filtration, carbon adsorption, and a suitable physical-chemical ammonia removal process.

The elimination of the bicarbonate alkalinity by biological nitrification in secondary treatment of wastewaters of moderate alkalinity (100 to 150 mg./liter as calcium carbonate) and, therefore, the reduction in lime dose and amounts of sludges from lime precipitation to typically 50 mg./liter of $Ca_5OH(PO_4)_3$ and 15 mg./liter of organic solids indicate a potentially improved conventional tertiary treatment system. The system would consist of primary sedimentation, secondary treatment with nitrification, lime precipitation with filtration for solids separation, and carbon adsorption with biological denitrification on the carbon columns.

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